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AN INNOVATIVE DC POLARIZATION METHOD FOR EVALUATING COATINGS

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ABSTRACT

A new coating evaluation technique based on electrochemical polarization of specimens with scribed defects was developed and evaluated as a method for assessing corrosion protection by coatings on metals. A unique scribe method was developed to create reproducible defects on the specimens in a manner such that the coating/metal interface was consistently exposed. Various organic and inorganic coating systems were examined on aluminum substrates in 3.5% NaCl solution. Electrochemical results were compared to standard coating evaluation techniques. Preliminary results indicate that this technique is useful for comparative evaluation of coating systems, and offers a number of advantages such as fast and quantitative measurements, good reproducibility and sensitivity.

INTRODUCTION

Coating systems, composed of an inorganic surface pretreatment along with an organic primer and topcoat, have been the prevalent

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method for protecting metallic structures against corrosion. These coating systems however are ever changing especially with the advent of stringent hazardous materials regulations. Along with the development of these new coating systems there is a need for a technique to rapidly evaluate their performance. Currently several electrochemical techniques have been used to evaluate coating system performances⁽¹⁻⁹⁾. Each of them however have their slight draw backs most of which being long time duration's for testing.

Factors influencing a coating system's performance are the metal substrate, the coating, the metal/coating interface, and the operating environment. In this study an evaluation technique which could effectively study these factors was developed and evaluated. The technique is based on electrochemical dc polarization of an metal/coating interface scribed as defect. Thus, several coating systems will be tested to establish electrochemical parameters which can be used to describe coating performance. The results will be also compared with standard non-electrochemical coating evaluation methods.

EXPERIMENTAL PROCEDURE

Instrumentation

The electrochemical scribe testing (EST) technique is carried out by running a potentiodynamic scan from the cathodic to anodic domain on the exposed metal/coating interface in a corrosive medium (electrolyte). The metal/coating interface is exposed by creating a circular scribed defect in the test specimen. A cross section of this scribed defect is as shown in Figure 1. This defect is produced mechanically using a unique device developed in-house and is shown in Figure 2. The purpose of making a circular scribe on the coated panel is to expose the metal/coating interface in omnidirection to the test medium for occurrence of interfacial corrosion. The circular geometry also eliminates problems of end-effects which are quite common to cross scribe, and probably represents a most severe defect geometry for accelerated testing.

The scribing device as shown in Figure 2 applies a constant force between the scribing tip and the test specimen. The constant force is controlled by the load applied to the spring by a weight (mass) as shown. Once the scriber tip comes in contact with the specimen, the tip is rotated to produce the circular scribe. The scriber cuts through the coating down into the metal substrate. The depth profile and notch radius of the scribe

are dependent upon the coating thickness and the nature of metal substrate. However, for a given metallic substrate the notch (scribe) geometry is fairly consistent and reproducible (Figure 1).

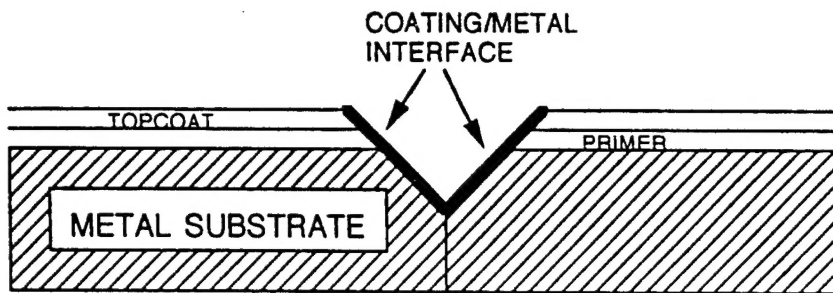


Figure 1: Cross section illustration of scribed defect.

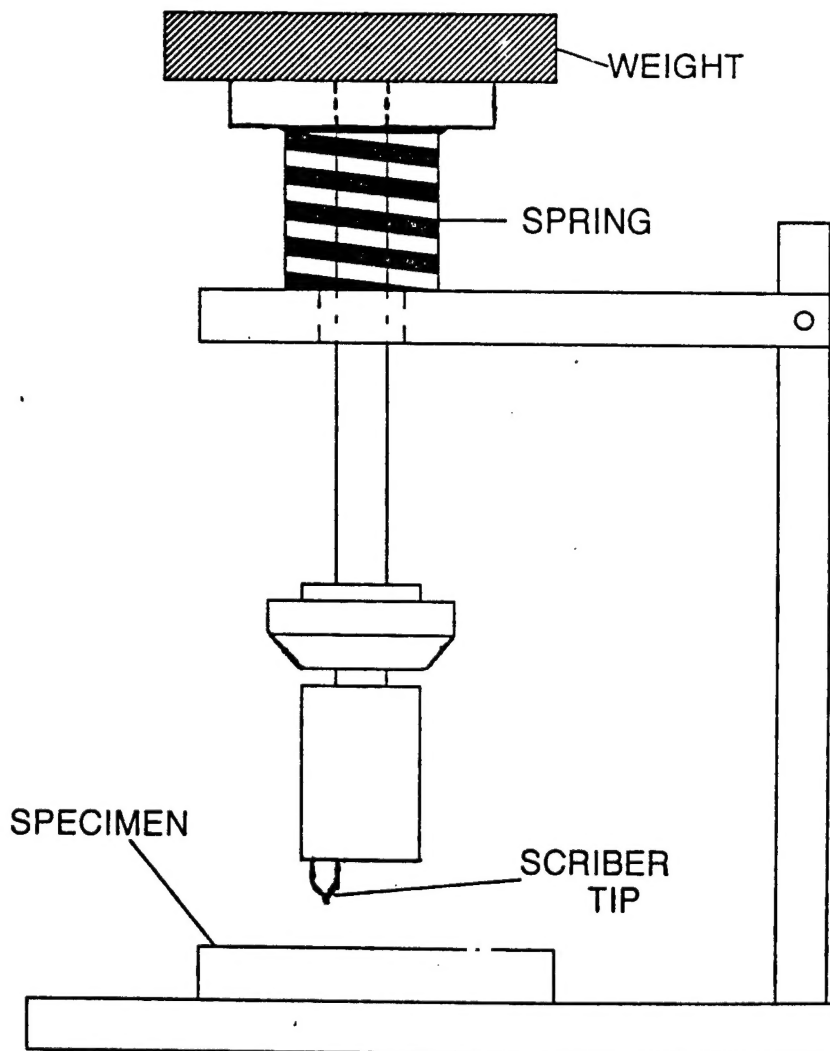


Figure 2: Schematic of scribing device.

Substrate and Coating Systems

Aluminum 7075-T6 alloy panels were used for evaluation of various pretreatments, primers and paints. Thus, panels were prepared using the following four coating schemes:

(1) Chromate Conversion Coated Aluminum Panels [Mil Spec No.]

- Top Coat Only [85285]
- Primer [23377] + Top Coat [85285]
- Self-Priming Topcoat (one-coat, unicoat)

(2) Tri-Chrome Conversion Coated Aluminum Panels

- Top Coat Only [85285]
- Primer [23377] + Top Coat [85285]
- Self-Priming Topcoat (one-coat, unicoat)

(3) Cleaned & Deoxidized Aluminum Panels

- Top Coat Only [85285]
- Primer [23377] + Top Coat [85285]
- Self-Priming Topcoat (one-coat, unicoat)

(4) Heavy Chromate Conversion Coated Aluminum Panels

- Primer [23377] + Top Coat [85285]

The protocol for specimen preparation includes the substrate preparation (conversion coating), primer (optional), and topcoat layers. A defect via the fore mentioned scribing technique was produced on the panels prior to exposure and testing. The interfacial area exposed consisted of the product of the length of scribed defect along coating thickness and the bare metal notch-width of the substrate.

Electrochemical Measurements

The electrochemical test cell consisted of a glass cylinder with an O-ring seal at one end mounted and clamped over the desired area of the test panel. The total exposed surface area created by this cell was $\sim 7.5 \text{ cm}^2$. The cell was then filled with approximately 50 ml of electrolyte. The counter electrode was a platinum disk with a hole in the middle to allow the capillary of the saturated calomel reference electrode tip to extend within 2mm of the specimen surface. The test cell configuration is illustrated in Figure 3.

The dc electrochemical polarization measurements were made using a Gamry CMS100 instrumentation system. The electrolyte used was a 3.5% NaCl solution (starting pH 6.25) and at room temperature (24°C).

Potentiodynamic electrochemical scans were run on the exposed area which included the scribed defect, from the cathodic to the anodic region. The scan was started at a preset -2.50 volts scanned to -0.50 volt versus the saturated calomel electrode (S.C.E.). A scan rate of 1.0 mV/sec was used to run the scans. The specimens were pre-exposed to the electrolyte solution for either 1,3, or 7 days prior to testing. Three to five redundant tests were run at each condition for statistical verification of reproducibility of the test.

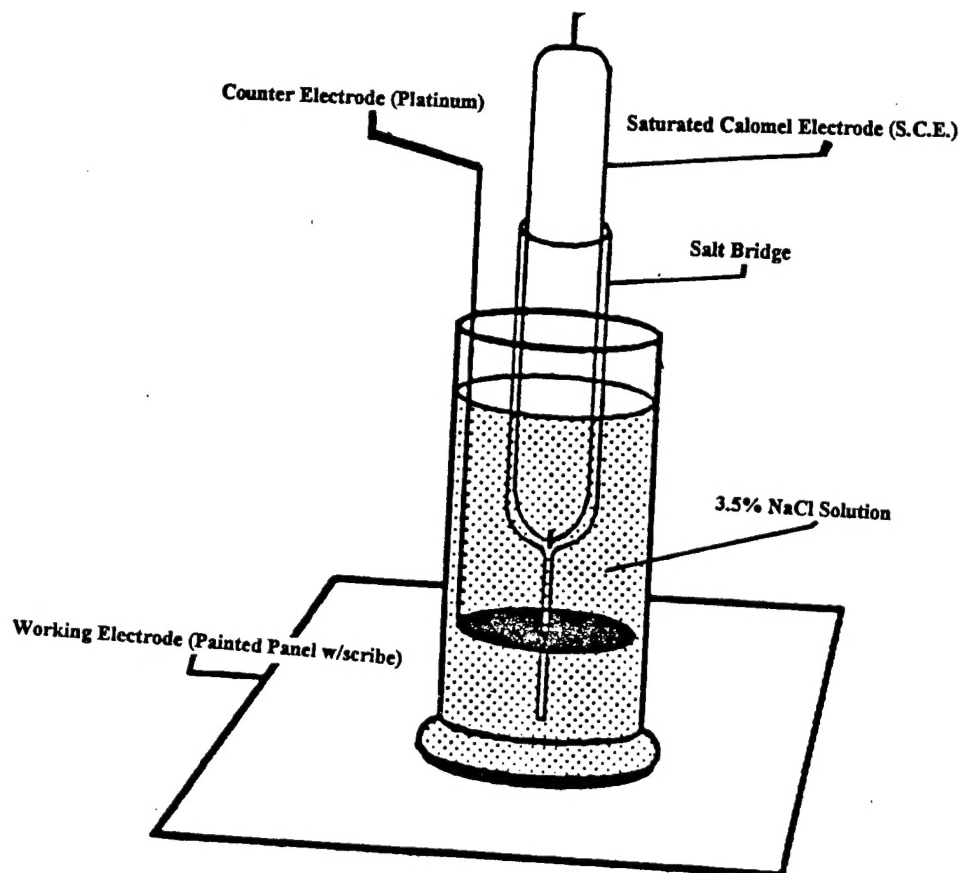


Figure 3: Electrochemical test cell

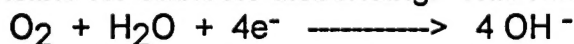
Salt Spray Exposure

Two sets of panels were scribed with a figure "X" through the coating into the metal substrate according to ASTM Standard Method D1654. The test panels were then exposed according to an ASTM Standard Method B-117 in salt spray environment and the test was run for 1000 hours. After testing, the panels were examined for debonding/lifting of the coatings and for corrosion product in the scribed area.

RESULTS AND DISCUSSION

The first set of experiments were conducted to determine whether the EST technique could distinguish between good and poor coating adhesion. Thus, prior to painting the aluminum panels were pretreated with (a) standard mil Spec (Mil-C-5541) chromate conversion coating (CCC) and (b) a heavy chromate conversion coating (HCCC). It is fairly well known that HCCC causes poor adhesion of the primer. The coating used on these test panels was a standard two coat system, a primer [23377] & topcoat [85285].

An examination of the cathodic regions of the potentiodynamic polarization diagrams, shown in Figure 4, show a large difference in the limiting current densities for the two pretreatments, i.e. current densities at potentials below -2.0V. When cathodic currents reach a limiting value, become independent of potential change, the reduction of oxygen becomes diffusion controlled. For the purpose of this study, a lower limiting current density value indicates lower availability of oxygen to the coating/metal interface, thus, lesser production of hydroxyl ions responsible for cathodic disbonding. This reaction can be written as



It is this production of hydroxyl ions that attacks the resin (paint system) and results in disbonding.

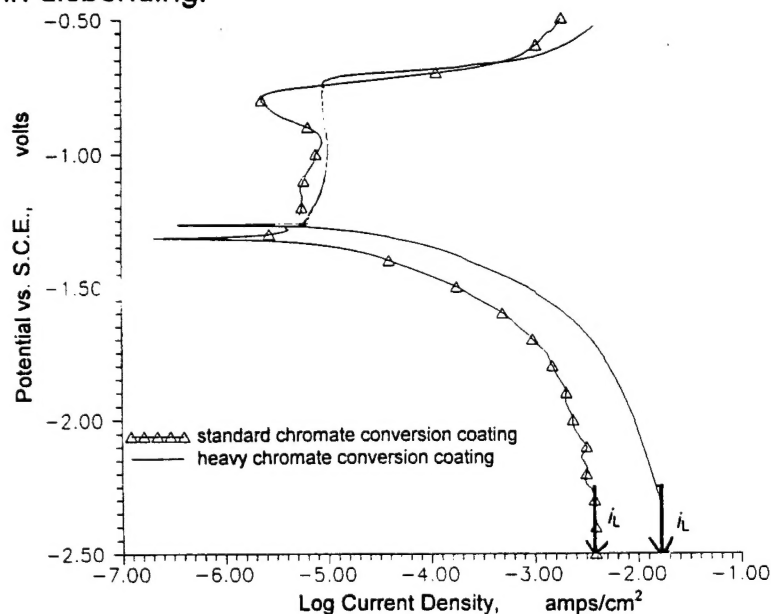


Figure 4: Polarization curves comparing surface pretreatments of a standard chromate conversion coating vs. a heavy chromate conversion coating under a Primer[23377] & topcoat[85285] paint system.

The results of salt spray exposure testing of these specimens are in agreement with those of EST. As shown in Figure 5, the CCC panels show no signs of adhesion loss or corrosion in the scribe area, where as, the HCCC specimens exhibit severe paint lifting and corrosion product all along the scribe. Most probably, the corrosion product in the scribe correspond to higher anodic currents observed in the passive domain the polarization curve.

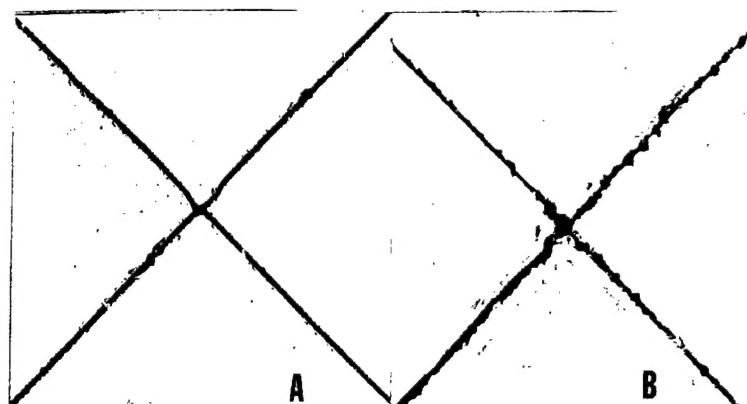


Figure 5: Photographs of primer[23377] & topcoat[85285] paint system with A) standard chromate conversion coating; B) heavy chromate conversion coating pretreatment after being scribed and exposed in 5% salt fog for 1000 hours.

The reliability of EST technique to evaluate and characterize the adhesion and corrosion resistant properties of the pretreatments (substrate preparation), both the standard two coat and a new one coat systems was selected. The two coat system again consisted of a standard primer [233 7] and topcoat [85285] while the one coat system was a formulation that meets a particular mil specification for a single coat paint system. In this study, the substrate preparation was either a simple cleaning and deoxidizing of the surface (CD) or a conventional chromate conversion coating (CCC). The third substrate preparation was a new trivalent chromium conversion coating (TCC).⁽¹¹⁾ The number 2 or 1 will be used after the acronyms for the surface pretreatment to identify two coat or one coat system, respectively.

The polarization curves on the two coat system (CCC2) specimens showed an interesting cathodic polarization behavior (cf. Figure 6). The limiting current density, i_L , for the CCC2 was higher than that for either TCC or CD2. As known conventionally, the CCC2 painted panels should

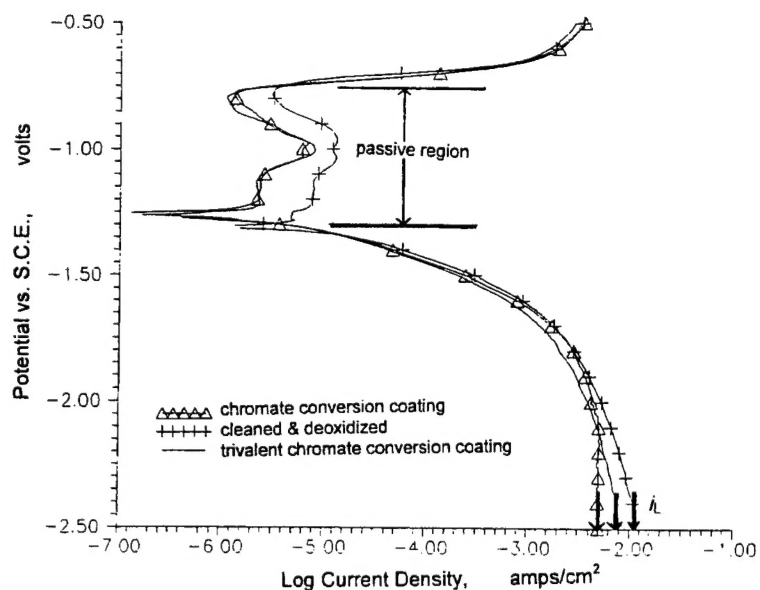


Figure 6: Polarization curves comparing surface pretreatments of a standard chromate conversion coating, trivalent chromium conversion coating and just cleaned and deoxidized under a Primer[23377] & topcoat[85285] paint system.

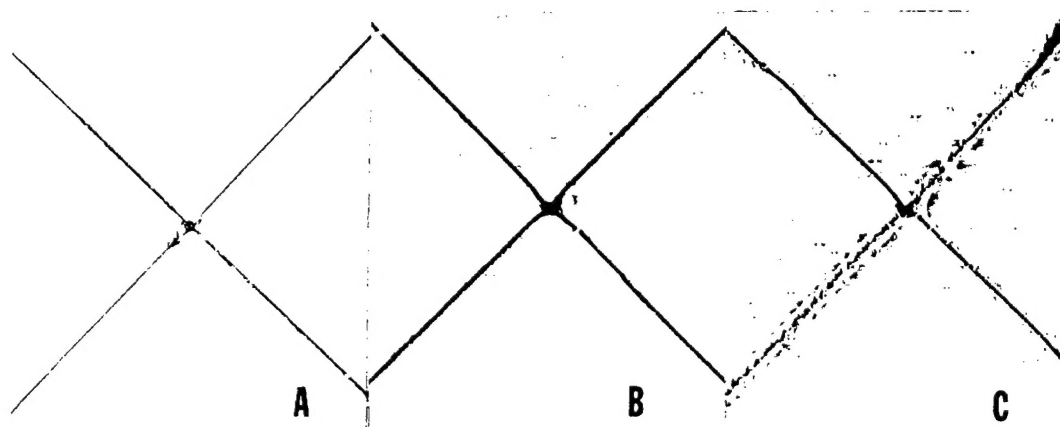


Figure 7: Photographs of primer[23377] & topcoat[85285] paint system with A) cleaned and deoxidized; B) trivalent chromium conversion coating; C) chromate conversion coating; pretreatment after being scribed and exposed in 5% salt fog for 1000 hours.

have lower i_L and perform the best. The CD2 and TCC2 had lower and identical current density in this region. As was also observed in Figure 4, an i_L value above 10^{-2} A/cm^2 could be an indication of a coating with an adhesion problem. The i_L for the CCC2 was approximately 10^{-2} A/cm^2 while the CD2 and TCC2 were at least a half decade lower. This difference of half a decade (5 m A/cm^2) could be an indication of a better adhesion of paint coating. This deduction was confirmed with the examination of the salt spray exposure specimens as shown in Figure 7, where plates A and B represent the pretreatments CD and TCC, respectively, and the plate C represents the CCC. A loss of paint adhesion is very evident along the scribe mark of the CCC2 panel while the TCC2 and CD2 panels show no significant signs of disbonding (cf. plates A and B with plate C in Figure 7).

In the case of one coat system, the i_L values of the cathodic polarization curves for the above mentioned three surface pretreatments separate themselves in following order, $\text{CD1} > \text{TCC1} > \text{CCC1}$ (cf Figure 8), i.e., the CCC1 treated panel showed the lowest and CD1 the highest i_L value. The worst being the CD1 panels followed by the TCC1 and CCC1 panels. However, none of them were much better than the other. Relatively speaking, the coating system which gives a lowest possible i_L values is better for adhesion and corrosion resistance. The polarization curve in the anodic domain, region of passivity, show a significant increase in the current density in the case of panel CD1 which did not have any inhibitor, i.e., cleaned and deoxidized surface. This difference could only be observed on one coat system (cf Figure 6 with Figure 8). The separation of curves in the anodic domain for the two coat system was indistinguishable. Since CD process does not contain any corrosion inhibitor in the bath, the corrosion of the substrate metal was quite obvious in the scribe area. The other two processes, CCC and TCC, contain Cr^{+6} and Cr^{+3} which serve as good corrosion inhibitors, thus, showed lower current densities. As before when these results are compared with the salt exposure tests, as shown in Figure 9, the results correspond well. Severe lifting and blistering was observed on the CD1 specimen, plate A. The TCC1 (plate B) and CCC1 (plate C) panels also showed some signs of poor adhesion with the TCC1 being slightly inferior, however no where to the extent of the CD1. Significant amount of corrosion product also appeared in the scribed area for CD1, while for the TCC1 and CCC1 specimens only slight corrosion product was evident.

If the polarization curves in Figures 6 and 8 are compared, it becomes quite evident that the two-coat system out performs the one-coat

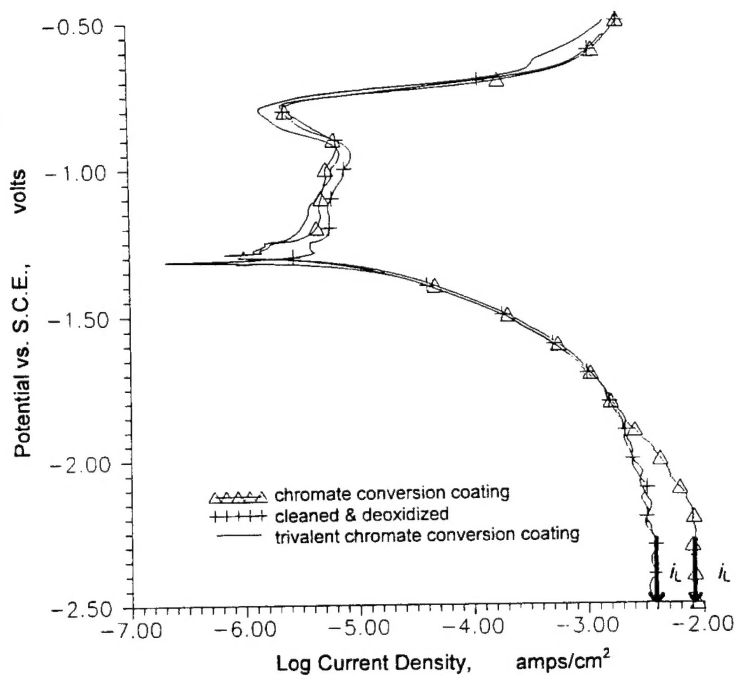


Figure 8: Polarization curves comparing surface pretreatments of a standard chromate conversion coating, trivalent chromium conversion coating and just cleaned and deoxidized under a Self-priming topcoat system (one-coat system).

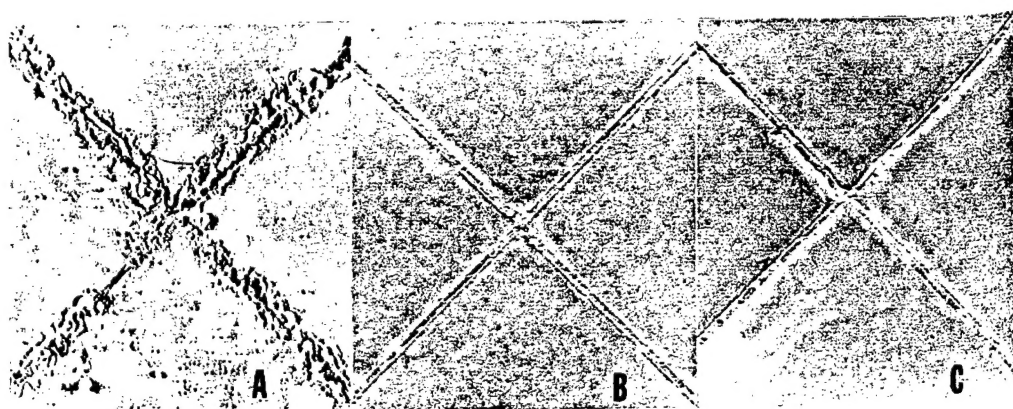


Figure 9: Photographs of Self-priming topcoat (one-coat) paint system with A) cleaned and deoxidized; B) trivalent chromium conversion coating; C) chromate conversion coating; pretreatment after being scribed and exposed in 5% salt fog for 1000 hours.

system. The anodic (passive region) currents from both sets of scans provide information which indicates that the two-coat system, including the cleaned and deoxidized surface, produces a decade lower current density than the one-coat system. Examination of the cathodic regions of both sets also predict greater adhesion problems with the one-coat system. These findings are well supported up by the results of salt exposure tests (cf. Figures 7 and 9).

Thus far it has been established that EST technique was able to show that different surface pretreatments had a great effect on the performance characteristics of the organic coatings. However, the corrosion inhibiting effects of the surface pretreatment were not fully confirmed as the coating system, both the primer and top coat, used always contained an inhibitor as an additive. Thus, new sets of panels pretreated as CD, TCC and CCC were prepared and coated with just a polyurethane topcoat containing no inhibitors. The reason for applying the topcoat for this testing was to prevent the pretreatment from leaching out into the electrolyte solution rather than migrating toward the scribed defect. The panels were electrochemically tested after one day pre-exposure in the test medium. The polarization diagrams obtained were as shown in Figure 10. They very clearly demonstrated that in the case of

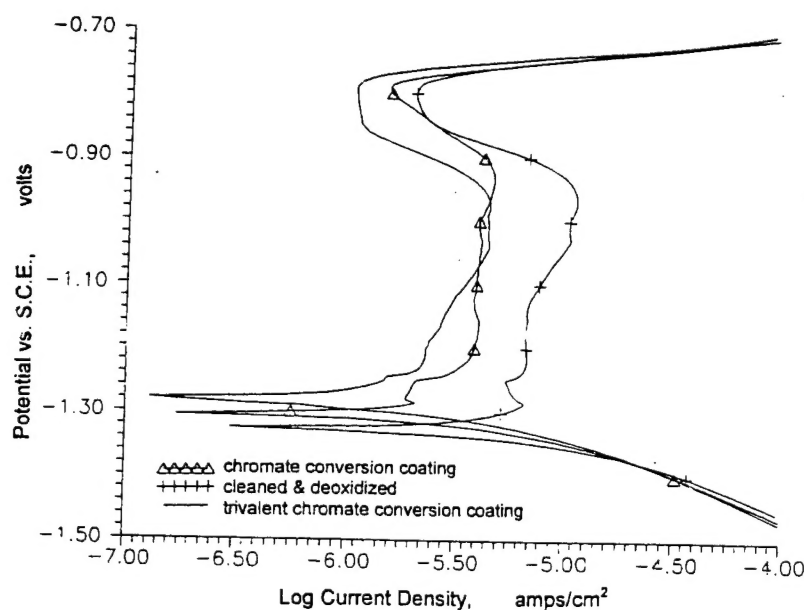


Figure 10: Polarization curves comparing the self-healing effects of chromate conversion coating and trivalent chromium conversion coating under an inhibitor free polyurethane topcoat[85285].

current density values, while they were highest for the cleaned and deoxidized specimen. The differences between passive regions of TCC and CCC were probably insignificant, although the currents appeared slightly lower for TCCC. In the cathodic domain the results were similar to those reported earlier; showed poor adhesion properties due to the fact they had only topcoat with no inhibitors. In actual salt exposure tests TCC and CCC specimens showed almost identical and least corrosion in the scribed area. Low corrosion current densities at anodic polarization potentials show that pretreatments have a self-healing effect on bare metal or the defect sites.

CONCLUSIONS

A novel scribing technique was developed to create reproducible defects on coated metal panels to characterize their corrosion and electrochemical behavior. The metal coating interface was studied through a potentiodynamic polarization method in which the interface was polarized from a very cathodic potential to a potential above open circuit in the anodic direction. The coating decohesion property was studied from the cathodic polarization effects and the corrosion resistance property of the substrate metal pretreatment was examined with respect to anodic polarization effects. The analyses of polarization curves was compared with the salt spray tests of the scribed panels. It was found that the values of limiting current densities, i_L , were directly related to metal-coating bond strength or adhesion, lower the i_L better the adhesion. This explanation was based on the understanding that interfacial cathodic reactions lead to oxygen reduction reactions and produce hydroxyl ions which attack the resin system to cause coating debonding. The corrosion resistance or passivating property of the pretreatments, conversion coatings, was related to values of the anodic currents in the passive region of the polarization curves, lower the current greater the resistance to corrosion.

Thus, the EST testing technique as described in this paper was found to be a valuable screening method for the assessment of corrosion protection properties of both the organic coatings and inorganic pretreatments (conversion coatings). It offers many advantages in the comparative evaluation of coating systems, such as quantitative measurements in relatively short test periods (compared to 1000 hour salt spray exposure testing), high reproducibility and sensitivity. The efforts are continued to further fine tune this method for routine testing.

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